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ORIGINAL PAPER

Modeling losses of copper-based fungicide foliar sprays in wash-off under simulated rain

P. Pérez-Rodríguez · M. Paradelo · D. Soto-Gómez · D. Fernández-Calviño · J. E. López-Periago

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Abstract Wash-off experiments of three Cu-based fungicides were conducted with a single raindrop simulator with known drop size and fall height. Losses were quantified as total Cu (Cu_T), in solution (Cu_L), and particulate (Cu_P). Cu wash-off time course was modeled for two different drop sizes using a stochastic model based on the cumulative detachment by random scattered raindrop impacts. In other set of experiments, the influence of raindrop size, fall height, and fungicide dose was analyzed statistically by means of a full factorial design. Most Cu was lost as particles sized from 0.3 to 1 μm. The stochastic model gave good estimations with two detachment performance levels. The best-fitting model parameters were as follows: the single element area covered by one impact (1.7 and 0.38 cm^2 for the large and small raindrop, respectively), the average number of repeated drop impacts on one single element area that exhaust non-rainfast fungicide (4.2 ± 3.0 small drops and 2.5 ± 0.5 large drops for the high performance level, low performance level needed 30 ± 10 large drops and 40 ± 88 small drops), and the mass washed-off by a single-drop impact (from 1.27 ± 0.2 μg Cu to 3 ± 1 ng Cu per impact). Factorial design showed the dosage was the most influential factor in the three fungicide formulations. The model can help to estimate fungicide losses in field from rainfall and canopy properties. However, the particulate/soluble loss ratio cannot be predicted by the model since both the particle detachment and solubilization were not clearly related with the raindrop energy.

Keywords Non-point source pollution · Copper fungicides · Rain fastness · Pesticide wash-off · Soil pollution

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P. Pérez-Rodríguez (✉) · M. Paradelo · D. Soto-Gómez · D. Fernández-Calviño · J. E. López-Periago
Área de Edafoloxía e Química Agrícola, Departamento de Bioloxía Vexetal e Ciencia do Solo, Facultade de Ciencias, Universidade de Vigo, 32004 Ourense, Spain
e-mail: paulaperezr@uvigo.es

M. Paradelo
Department of Agroecology, Faculty of Science and Technology, Aarhus University, Blichers Allé 20, P.O. Box 50, 8830 Tjele, Denmark

D. Fernández-Calviño
Department of Plant and Environmental Science, University of Copenhagen, Frederiksberg, Denmark

Introduction

Copper-based fungicides are used to prevent fungal diseases on a variety of crops. Their extensive use since the late nineteenth century has led to substantial accumulation of Cu in vineyard soils (Fernández-Calviño et al. 2009), where the element has reached phytotoxic levels in some cases (Komárek et al. 2010). There have also been reports of high Cu concentrations in soils bearing other crop types (Lima 1994; Schramel et al. 2000; Loland and Singh 2004; Van Zwieten et al. 2004).

This trend is likely to persist but will depend on the application rate of copper sulfate, oxychloride, and oxide, which are on the EU list of agriculturally allowed products (Official Journal of the European Communities 2009). In fact, using these Cu products is allowed in organic farming regulations in the EU (Official Journal of the European Communities 2008). Therefore, a deeper knowledge of the processes governing the wash-off of Cu-based fungicides is required to improve their efficiency and to minimize their damage to the environment.

Rainfall wash-off tests have been used in rain fastness and rainfall tenacity studies of several plant protection substances: foliar deposits of commercial formulations of diflubenzuron (Sundaram and Sundaram 1994), carbaryl (Willis et al. 1996), chlorothalonil (Wauchope et al. 2004), phosmet (Hulbert et al. 2011), glyphosate commercial formulations (Gannon and Yelverton 2008), bio-herbicides (Boyette et al. 2012), and fungicides such as dimethomorph, chlorothalonil, and mepanipyrim fungicides (Choi et al. 2009). The influence of surfactants on the tenacity of tribenuron-methyl (Pannacci et al. 2010), the sticker adjuvants based on organosilicone/latex added to fungicides (Gaskin and Steele 2009), and the effect of seed oil ethoxylate surfactants on the tenacity of the mancozeb (Hunsche et al. 2008) were also studied using rainfall tests. The wash-off of Cu-based fungicides may reduce their efficiency. Development of formulations for reducing off-target deposition requires a better understanding of the mechanisms behind the wash-off of leaf sprayed fungicides. Studies on the influence of water-sweeping energy on the tenacity of Cu-based fungicide sprays revealed a relationship between Cu losses and the energy of the water layer moving on the fungicide resting on the sprayed surface (Paradelo et al. 2008). Researchers found Cu losses in the form of suspended particles, which exposed the significance of the mechanical effect of particle sweeping during wash-off (Otero et al. 2003; Paradelo et al. 2008). These soluble and particulate Cu can accumulate in soil surface or migrate to subsurface through macropores (Kazemi et al. 2009; McGrath et al. 2010; Michel et al. 2010).

However, further experimental data are required to determine the influence of raindrop energy on Cu wash-off. Additional factors significantly influencing Cu wash-off losses include some properties of the fungicide formulation. The active ingredients and adjuvants in fungicide formulations affect their environmental behaviors (Pose-Juan et al. 2011). Rainfall characteristics, impact energy, raindrop size, and accumulation of impacts on the leaf surface are factors that can be important in studying fungicide wash-off. Calder's model for rainfall interception by the canopy (Calder 1986) may be a good starting point for modeling the dynamics of fungicide loss by rainfall. The model can provide a link between the intensity of the fungicide wash-off and the rainfall event characteristics, such as duration, intensity, and raindrop size distribution. Previous work (Pérez-Rodríguez et al. 2013) showed that a Calder's based wash-off approach gives good estimations of Cu losses in sprayed potato leaves.

The objectives of this work were as follows: (1) to test a stochastic model to examine the experimental results of Cu loss rate in wash-off obtained with the single-drop rainfall wash-off simulator in a synthetic surface and (2) to study the distribution of Cu losses between the dissolved and solid particle fractions and to determine the influence of the fungicide dosage, drop size, and drop fall height on Cu wash-off losses with three commercial Cu-based fungicides.

This study was carried out in the Ourense province (Spain) during the year 2012.

Materials and methods

Fungicides

Three commercial formulations of Cu-based fungicides were studied, one containing copper calcium sulfate (Bordeaux mixture, BM) and two Cu oxychloride formulations, (copper oxychloride, CO), and a mixture of copper oxychloride and propylene glycol (CO–PG). Their characteristics are summarized in Table 1. The Cu contents of the three fungicides were determined in quintuplicate by digestion to complete dissolution of the sample in aqua regia (Hossner 1996). The particle sizes were measured by laser dispersion scattering with a Zetasizer Nano (Malvern Instruments, Ltd., UK).

Rain simulator

Figure 1 and pictures in supplementary information depict the experimental setup described in both modes for collection system, and the raindrop simulator which consisted of a single-drop dripper with a KDS-270-CE pulseless high precision pump from KD Scientific (Holliston, MA, USA) fitted with a 20-mL syringe connected to the dropping system with 1/16″ o.d. PTFE–polypropylene tubing. The influence of small and large raindrops was studied in the wash-off tests.

Random scattering was controlled by a 3-axis computer numerical control machine (CNC) (Redonda TS1313B, China). The dripper was attached to the CNC machine, and random drop impact coordinates were generated by a computer code. Coordinates were transferred to the CNC machine by Mach 3 CNC controller software. This was able to control the velocity of the X and Y axes accordingly the drop frequency, providing a uniform random scattering of the drop impacts on the sprayed surface. The impact locations coordinates were circumscribed into a circle of 4 cm in diameter.

The drop size was adjusted and used for both modes by selecting appropriately flat ending calibrated needles.

Table 1 Specifications of the commercial fungicides used

Fungicide	BM	CO	CO–PG
Composition	Bordeaux mixture, wetting powder, 20 % Cu	50 % Copper oxychloride, wetting powder	65.4 % Copper oxychloride, 2.01 % 1,2-propanediol in aqueous suspension (density 1.94 g cm^{-3})
Concentration (kg L^{-1})	0.20	0.40	0.29
CAS no.	8011-63-0	1332-40-7	1332-40-7, 57-55-6
Chemical formula	$CuSO_4 \cdot 3Cu(OH)_2 \cdot 3CaSO_4$	$CuCl_2 \cdot 3Cu(OH)_2$	$CuCl_2 \cdot 3Cu(OH)_2$, $C_3H_8O_2$
Dominant mineral phases	Chalcanthite	Atacamite	Atacamite
log_K[a]	−2.64	−7.391	−7.391
Mean particle size (µm)	0.902	0.979	0.315
[Cu] in Fungicide (mg g^{-1})	222 (1.1)	535 (2.8)	462 (1.8)

Standard deviations are in parentheses

[a] Solubility constant (Manion et al. 2008)

Small drops (equivalent diameter of 2.625 ± 0.0032 mm, CV = 0.12 %) were obtained with a thin needle (Hamilton Europe 8648-01, 25 s/1.97″/3, 6/PK, NDL, Switzerland), and large ones (equivalent diameter of 3.787 ± 0.021 mm, CV = 0.55 %) were obtained with a thicker needle (Rheodyne 3725-056 1/16 Peek Needle, from IDEX Health and Science, Oak Harbor, WA, USA). The equivalent diameter, fall velocity at the impact point, and kinetic energy of the drops were calculated for 1 and 2.5 m fall heights (Epema and Riezebos 1983). These sizes can be found in moderate to heavy rains (Byers 1959; Rogers and Yau 1996; Pruppacher and Klett 2010). The raindrop intensity was set to 14 mm h^{-1} in all experiments.

Wash-off setup

Wash-off experiments were performed by impinging the drops on an artificial surface sprayed with the fungicides. The inner side of a polypropylene beaker was the surface supporting the fungicide (Fig. 1). The properties of the polypropylene beaker used as a leaf surface simulator, identical to that used in a previous study, have been discussed elsewhere (Paradelo et al. 2008).

Rainfall simulator was used in two modes of operation: (a) Random rotating mode in which random impacts were applied on sprayed surface in rotation. Therefore, drop impacts covered a larger area of the spray surface. This mode was used in the factor analysis because it has a greater impact area minimizing the pesticide exhaustion effects on the dynamics. (b) The random non-rotating mode was used in the calibration of the stochastic model that simulates the exhaustion of the sprayed fungicide.

In the rotating mode, the beaker was connected via an axle to a variable-speed electrical motor to facilitate uniform distribution of the drops on the impact surface. The axle was tilted to ensure that the drops would impinge at an angle of 45° on the surface supporting the fungicide. This angle falls within the typical range of leaf inclination angles in many crops, allowing both splashes and the fungicide released from the impact surface during each wash-off run to be collected in the bottom of the beaker.

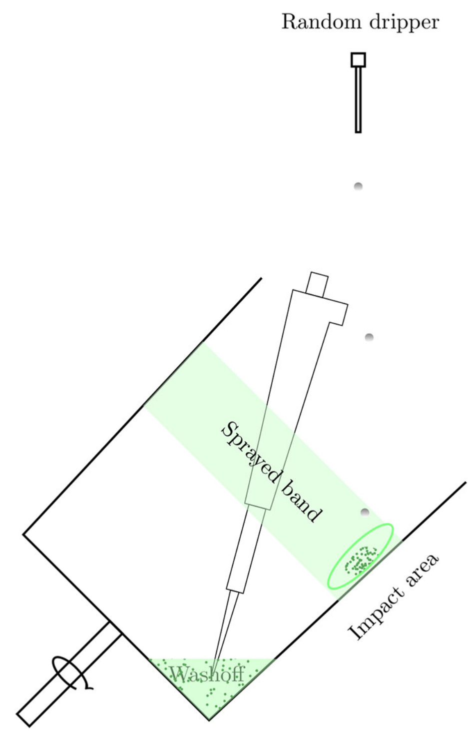

Fig. 1 Schematic depiction of the single raindrop wash-off simulation system used in the fungicide loss experiments. Raindrop falling from the dripper and washing-off the fungicide and fungicide collection system

The fungicides were sprayed on a target, a ring with a 34 cm circumference × 3.5 cm wide inside the beaker. A width of 3.5 = 2.5 cm/cos 45° was given by the scattering diameter of the raindrops (i.e., near 2.5 cm) and the impinging angle. The dosage and rainfall intensities were calculated for the horizontal projected surface area (85 cm^2). In the non-rotating mode the drop impinging area covered a circle of 4 cm in diameter, the angle of the axle was the same as in the rotating mode.

The suspensions were prepared by mixing each product at the manufacturer's recommended concentration (Table 1) with distilled water. All suspensions were mixed vigorously prior to spraying on the testing surface. After spraying, the fungicide deposit was air-dried at 25 °C for 48 h. Scanning electron microscopy SEM (Jeol JSM-6700F, Jeol Ltd. Tokyo, Japan) was used to examine the fungicide deposited in the beaker. Specimens of the beaker walls were cut and shaded with carbon before examination. Elemental composition of deposits was determined by X-ray microanalysis probe of the SEM (Supplementary information).

Losses by spray drift were accounted for in the mass balance calculations of fungicides in the wash-off experiments, being multiplied by their respective spraying efficiencies. The spraying efficiency was calculated as the mass of Cu sprayed by the nozzle divided by the mass of total Cu in the beaker.

Following each wash-off run, the fungicide was re-suspended by agitation (Fig. 1), and one half of the wash-off volume (10 mL) was directly vacuum-filtered across a nitrocellulose membrane of 0.45 µm pore size to determine Cu_L. The other half (10 mL) was acid-digested to determine Cu_T. The particulate Cu was calculated as $Cu_P = Cu_T - Cu_L$. This procedure was carried out in the same way as Pérez-Rodríguez et al. (2013).

The Cu_T was measured after complete dissolution of the fungicides attached to the beaker using aqua regia. All Cu concentrations were measured by flame photometry with a Solaar-M5 air–acetylene spectrometer from Thermo Fisher Scientific, Inc. (Waltham, MA, USA).

Kinetic loss in wash-off

Kinetic experiments were performed according to Pérez-Rodríguez et al. (2013) to examine the rate of fungicide loss and the influence of the raindrop size. After each 1 mL of rainfall, all the washed-off suspension was pipetted from the bottom of the beaker. Each 1 mL fraction was digested and analyzed to measure the Cu_L and Cu_T. The raindrop fall height was 2.5 m. The cumulative loss of Cu as a function of the simulated rainfall volume was recorded.

Model of fungicide loss

The sprayed surface can be divided in a discrete number of equal elements areas. Assuming that the impact locations of the raindrops in a finite surface is randomly independent and identically distributed, the probability density function of the occurrence of a number of raindrop impacts in a elementary area surface would have to obey a Poisson distribution. Using this approach, Calder (1986) developed a stochastic model based on a Poisson distribution function to describe the wetting of vegetal cover by rain. From a mathematical point of view, the accumulation of intercepted rainfall on leaves and pesticide losses by wash-off as a result of the accumulation of raindrop impacts causing detachment of the fungicide can be formulated mathematically in the same way. Therefore, our model assumes that the mass of fungicide lost by a single impact on the same location is constant until repeated impacts in the same element area surface had exhausted all the non-rainfast fraction of the fungicide in this element. The raindrop performance in the fungicide detachment depends on a variety of factors, including the attachment force of the fungicide to the leaves, the drop impinging angle, the amount of water stored in the leaf surface, and the fungicide solubilization rate. To take into account some of this variability, two detachment performance levels were considered for the same drop. Thus, the model can be described as follows: A surface sprayed with a fungicide can be divided into a number (L) of equal elementary areas, each with the same probability of being hit by a raindrop. The number of drops falling during a rainfall episode (k) divided by the number of elements that compose the surface is $k/L = m$. Therefore, the cumulative probability that a unit surface element receives at least a number of raindrop impacts (r) can be approximated by:

$$\sum_{i=0}^{r} P_i = \exp(-m) \sum_{i=0}^{r} \frac{m^i}{i!}. \quad (1)$$

The probability that an element is hit by more than r drops is:

$$1 - \sum_{i=0}^{r} P_i. \quad (2)$$

If q_j is the maximum number of impacts exhausting at the performance level j in a single element, then the number of drops causing complete detachment of the fungicide in a surface in an episode with r raindrop impacts per element is:

$$Q_j = \left(1 - \sum_{i=0}^{r} P_i\right) q_j + (i - q_j) \exp(-m) \sum_{i=0}^{r} \frac{m^i}{i!}. \quad (3)$$

The first term on the right side represents the contribution of all the elements that have received at least r impacts, which are necessary to cause the maximum loss at j level from a single element. The other terms represent the contribution of the elements that have received less than r impacts. The number of impacts in the wash-off experiments was calculated by dividing the rainfall volume in a run by the volume of a single drop.

If the pesticide loss at j level in an elemental area is determined by the number of effective impacts, n is the mean number of effective raindrop impacts per element that produce a loss of fungicide:

$$n_j = q_j[1 - \exp(-m)] + \exp(-m)\sum_{i=0}^{r}(i - q_j)\frac{m^i}{i!}. \qquad (4)$$

A single element receiving a number of impacts greater than q_j would not cause increased loss of the fungicide fraction at j level, so n is the number or repeated impacts in the same element that contribute to the loss of fungicide before exhaustion of the fungicide reservoir per unit area. Finally, the total mass of fungicide lost in the wash-off assuming two performance levels is given by their summation:

$$M = nL\sum_{j=1}^{2} M_j, \qquad (5)$$

where M_j is the mass of the pesticide lost per element, the subscript j accounts for the mass washed-off at a specific performance level. In this work, j accounts for two washing-off performance levels (i.e., different tenacity of the fungicide) namely 1 and 2, and L is the number of surface elements in the sprayed surface area. This approach allows modeling the fungicide wash-off rate using the influence of individual raindrop impacts accumulated on a surface sprayed with a fungicide. The relationship between the loss of fungicide and the impact of raindrops was performed by fitting Eqs. 4 and 5 to the experimental wash-off kinetics data. The fitting parameters were L, q_j, and M_j. The model was written in FORTRAN and linked to the Levenberg–Marquardt nonlinear optimization package LM-OPT (Clausnitzer and Hopmans 1995) to perform the fittings.

Wash-off factor design

A full factorial orthogonal design 2^3 with five replicates was used (with high values coded as + and low values coded as −) to examine the influence of the factors fungicide dosage (1 and 2 mL of fungicide suspension), drop size (2.63 and 3.79 mm), and fall height (1 and 2.5 m). The response variables were the amounts (mg) of Cu_L, Cu_P, and Cu_T in the washed-off water, and their respective percentages of total mass of Cu sprayed under the drop impinging area. The optimum experimental conditions of the rainfall simulator in the factor analysis were rainfall intensity of 14 mm h^{-1} lasting 10 min (3.3 mm total rainfall per run).

The influence of each individual factor, the potential interactions between factors, and the prediction model were assessed by statistical tests (Box et al. 1978; Akhnazarova and Kafarov 1982).

An analysis of variance (ANOVA) was applied and the consistency of the factorial design was verified by Fisher's F test ($\alpha < 0.05$). The significance of coefficients of the models was calculated using Student's t test ($\alpha < 0.05$) as the acceptance criterion.

Results and discussion

Spraying

The SEM images of the dried traces of the fungicides sprayed in the beaker (See supplementary information) showed the distributed droplets ranging from 0.05 to 2 mm in diameter. The traces of dried fungicide accumulated in rings due to the effects of capillary and gravity forces. Overlapping of particles occurred mostly at the border of the rings. Inside the ring, the distribution of particles was sparse, and they were directly attached to the beaker. The images of BM showed very angular shaped crystals of $CuSO_4$ (light tone in back scattering electron images) near 1 μm size, and $CaSO_4$ more rounded and bigger particles (darker tone in back scattering images). The images of BM also showed crystals of $CaSO_4$ that precipitated during drying. The most of CO particles accumulated at the borders of droplets, and the crystals were near 1 μm size. The CO–PG showed that particles were smaller in size and were embedded in an organic matrix forming clumps. The SEM images showed that all fungicides were heterogeneously distributed over the surface, either directly attached to the support or forming piles. Therefore, the effectiveness of fungicide detachment would vary depending on the type of arrangement of particles. SEM photographs of Cu-based fungicides sprayed on potato leaves show this type of particle arrangement (Pérez-Rodríguez et al. 2013).

Simulated rainfall

The characteristics of the artificial rain and other experimental conditions in the wash-off experiments are summarized in Table 2. The terminal velocity (i.e., drip point placed at infinite height) was calculated according to Epema and Riezebos (1983). Table 2 shows the impact energy ranges calculated by comparing the experimental conditions with estimates obtained under terminal-velocity conditions for the two raindrop sizes. The small drops falling from a height of 2.5 m possessed more energy than the large drops falling from 1 m.

Table 2 Physical properties of the raindrops obtained by the simulator in the wash-off tests

H (m)	*S* (mm)	*V* (m s^{-1})	DE (J)	E_1 (J)	E_2 (J cm^{-2})
1.0	2.62	4.0	1.7×10^{-4}	3.57×10^{-1}	4.20×10^{-3}
1.0	3.79	4.1	5.1×10^{-4}	3.60×10^{-1}	4.25×10^{-3}
2.5	2.62	5.7	3.8×10^{-4}	8.10×10^{-1}	9.55×10^{-3}
2.5	3.79	6.0	1.2×10^{-3}	8.56×10^{-1}	1.01×10^{-2}

H falling height, *S* drop size (diameter), *V* drop velocity at impact, *DE* drop energy, E_1 total energy per run, and E_2 energy per surface area in a run

Rate of fungicide loss

Time course Cu loss in the kinetic wash-off experiments was initially tested for CO fungicide (Fig. 2). With the small droplet size (2.6 mm in equivalent diameter, Fig. 2a), there was a fast loss rate of 50 µg Cu after the first 10^3 impacts (equivalent to 6 mg Cu m^{-2}, with 1.18×10^5 impacts m^{-2}, 0.051 µg Cu per impact), followed by a slower rate with a total loss of 80 µg Cu after 12,685 impacts (9.4 mg Cu m^{-2}, 1.51×10^6 impacts m^{-2}, 6.5 ng Cu per impact).

With the large raindrops (3.8 mm in diameter, Fig. 2b), the loss rate in the initial stage was even faster than that observed for the small raindrops, with 650 drops yielding a loss of 160 µg Cu (18.8 mg Cu m^{-2}, 7.65×10^4 impacts m^{-2}, 0.25 µg Cu per impact). At the end of the second stage, the total loss was 0.205 mg Cu after 4,226 impacts (24.4 mg Cu m^{-2}, 4.97×10^5 impacts m^{-2}, 49 ng Cu per impact).

The two-stage behavior suggests that two wash-off performance levels contribute to the total loss of fungicide. In the first stage, detachment of some fungicide particles that were loosely attached to the beaker prevailed resulting in a high performance level. However, in the second stage, solubilization of fungicide particles, either remaining attached to the baker or suspended in washed-off water, predominated. The Cu fractionations in samples collected at early and late times were compared. The first fractions had more Cu_P than the last fractions, which mainly contained the soluble forms.

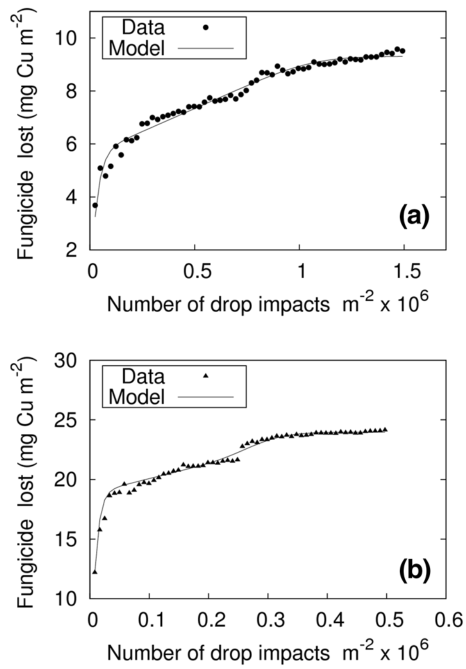

Fig. 2 Time course of the CO fungicide lost during a simulated rainfall. Data expressed as mg of total Cu per square meter of sprayed surface. Points represent experimental data, and line the best fitting stochastic model. **a** Data obtained with the small raindrop. Raindrop size is 2.6 mm. **b** Data obtained with the large raindrop. Raindrop size is 3.8 mm

Modeling of the wash-off kinetics

Stochastic modeling was performed by fitting the model parameters to the experimental loss rate. The parameters were the number of elements on the sprayed surface (L), the efficiency of detachment per impact M_j (i.e., micrograms of Cu released per element), and the number of repeated impacts for the same element that exhaust the reservoir of fungicide (q_j) for two performance levels $j = \{1, 2\}$. The size of an elemental area was given by the area of the influence of a splash produced by a single raindrop (i.e., area where detachment by the impact takes place); consequently, the number of elemental areas in the target (L) depended on the average size of the raindrop splash influence. The fitted parameters (Tables 3, 4) indicate that the optimum number of elements in the target was 68 ± 92 for large raindrops and 254 ± 79 for small raindrops. The values of these parameters show a rather large uncertainty. Appropriate values used for all fungicides were set of $L = 50$ (large drop) and $L = 223$ (small drop), these values corresponded to impact surface areas of 1.7 and 0.38 cm^2 for the large and small raindrop, respectively. Overall fitting of q_1 for all fungicides was $q_1 = 2.5 \pm 0.5$ impacts (large) and $q_1 = 4.2 \pm 3.0$ impacts (small). These were used as part of the initial parameter set to fit the rest of parameters of Calder's model. For the low performance

Table 3 The best-fitting parameters (mean ± SD) used to predict the copper fungicide loss to the single large raindrop simulator

Fungicide formulation	M_1	q_2	M_2	ME	RMSE
In solution					
BM	0.007 ± 0.007	29.8 ± 13.3	0.008 ± 0.005	0.996	0.004
CO	0.053 ± 0.035	34.2 ± 14.6	0.037 ± 0.001	0.999	0.001
CO–PG	0.03 ± 0.064	39.5 ± 15	0.036 ± 0.008	0.997	0.004
Total					
BM	0.163 ± 0.035	26.7 ± 6.4	0.023 ± 0.007	0.996	0.003
CO	0.975 ± 0.146	36.8 ± 14.8	0.107 ± 0.027	0.999	0.001
CO–PG	1.274 ± 0.198	28.6 ± 8.9	0.143 ± 0.048	0.994	0.003

L is the number of elements in the surface fixed in 50; *q* is the number of effective impacts (being fixed q_1 2.5 ± 0.5); *M* is the mass detached in a single surface element (µg of Cu released per element and raindrop impact); *ME* is the model efficiency coefficient; and *RMSE* is the root mean square error. The model is the two-stage version. Subscripts denote the values for stages 1 and 2

Table 4 The best-fitting parameters (mean ± SD) used to predict the copper fungicide loss to the single small raindrop simulator

Fungicide formulation	M_1	q_2	M_2	ME	RMSE
In solution					
BM	0.004 ± 0.003	94.8 ± 284.3	0.003 ± 0.001	0.989	0.007
CO	0.112 ± 0.024	40 ± 1	0.021 ± 0.004	0.991	0.005
CO–PG	0.018 ± 0.01	40 ± 97.5	0.009 ± 0.002	0.995	0.005
Total					
BM	0.028 ± 0.006	40 ± 84.8	0.005 ± 0.001	0.993	0.004
CO	0.234 ± 0.036	40 ± 90.6	0.03 ± 0.006	0.987	0.005
CO–PG	0.164 ± 0.029	40 ± 1	0.024 ± 0.005	0.995	0.003

L is the number of elements in the surface; *q* is the number of effective impacts fixed in 223; *q* is the number of effective impacts (being fixed q_1 4.2 ± 3.0); *M* is the mass detached in a single surface element (µg of Cu released per element and raindrop impact); *ME* is the model efficiency coefficient; and *RMSE* is the root mean square error. The model is the two-stage version. Subscripts denote the values for stages 1 and 2

level average values increased to $q_2 = 30 \pm 10$ for large drops and $q_2 = 40 \pm 88$ for small drops, standard errors include the influence of the fungicide type.

The best-fitting parameters (M_1, q_2, and M_2) for each fungicide are shown in Table 3 for large raindrop and Table 4 for small raindrop. The predicted values obtained in each fungicide are represented as lines in Fig. 3 for Cu_L and Cu_T and for each raindrop size. This model also allowed us to examine the two stages individually by modeling the two performance levels separately. The effectiveness at the high performance level M_1 (µg Cu per element) for Cu_T for each of the three fungicides was 0.16 ± 0.04 BM, 0.98 ± 0.15 CO, and 1.27 ± 0.2 CO–PG for the large raindrop and 0.03 ± 0.01 BM, 0.23 ± 0.04 CO, and 0.16 ± 0.03 CO–PG for the small raindrop. The large/small raindrop ratios for M_1 were approximately 5.8, 4.2, and 7.8 for BM, CO, and CO–PG, respectively. For the second performance level, M_2 for the large drop was 0.02 ± 0.01, 0.11 ± 0.03, and 0.14 ± 0.05 µg per element. For the small drop, M_2 was 0.01 ± 0.001, 0.03 ± 0.006, and 0.02 ± 0.005 µg for BM, CO, and CO–PG, respectively. Differences in performance levels were lower for small raindrops than for large ones. According to this model, the performance in the fungicide loss induced by detachment of particles is much greater at early stages than in late stages, and solubilization predominates in late stages. The two performance levels model is supported by the work of Paradelo et al. (2008), which showed a significant contribution to fungicide losses by slow solubilization of Cu oxychloride by wash-off. The results obtained here with artificial rain were not sensitive to the fall height even in the high performance level. Therefore, the effectiveness of producing losses seems to be more dependent to the accumulation of raindrop impacts than their power. The potential application of this model to field cases depends on the way of how to approach the variations of the drop size and energy of the natural rainfall and the canopy. Candidate methods can include Monte-Carlo simulations to model the uncertainties associated to the natural scenarios.

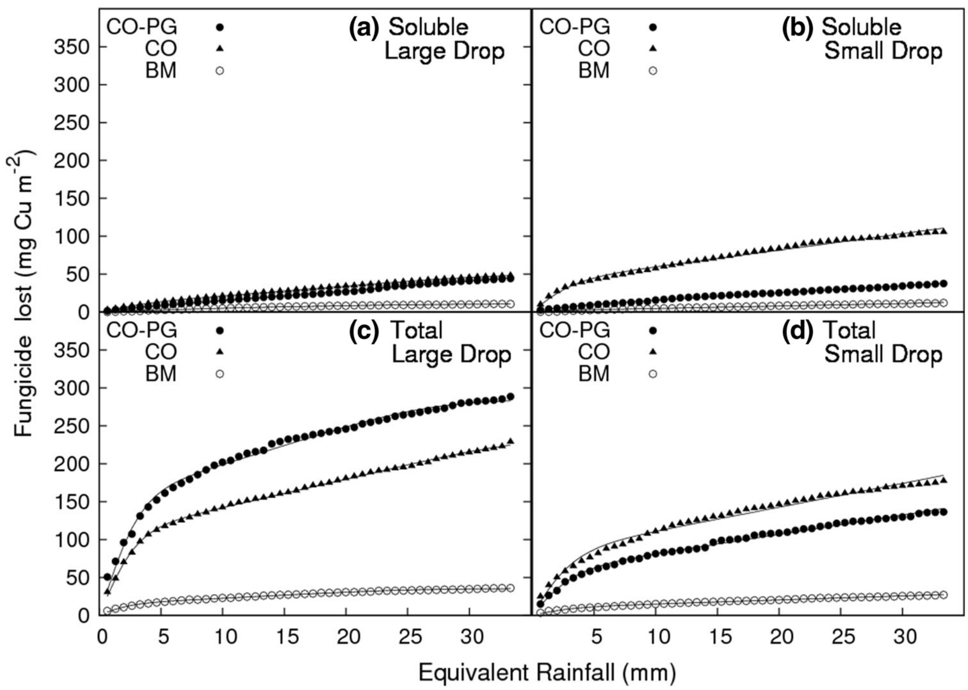

Fig. 3 Time course of each fungicide lost during a simulated rainfall. Data expressed as mg of total Cu per square meter of sprayed surface. Points represent experimental data, and line the best fitting stochastic model. Data obtained in soluble fraction: **a** using the largest raindrop **b** using the smallest raindrop; data obtained from total Cu fraction: **c** using the largest raindrop **d** using the smallest raindrop

Factor analysis

The factor design was analyzed for Cu_L, Cu_P, and Cu_T. Calculations were made with the absolute mass (mg Cu lost in wash-off) and for the percentage of the washed-off mass relative to the mass of Cu sprayed. For all fungicides, the Cu_T lost, expressed as a percentage, was not statistically influenced by any of the factors. With regard to the net losses (i.e., milligrams of Cu_T lost in a run), the only significant factor was the dose (*D*). The size of the raindrops (*S*) and fall height (*H*) were only statistically significant for Cu_L and Cu_P. The results were examined in detail for each of the three fungicides, BM, CO, and CO–PG. Figure 4a shows the Cu lost as particles for each of the three formulations and Fig. 4b summarizes the results of the total concentration of copper in the wash-off after a run. The losses were significantly different for the three fungicides, with means of 0.5, 4.5 and 2.5 mg Cu L^{-1} for BM, CO-PG and CO respectively. Figure 5 displays the ratio of CuP and CuL based on the total mass sprayed.

Bordeaux mixture (BM)

In the case of BM, the average loss of Cu_T (i.e., in the center of the factorial design) was 7.3 mg Cu m^{-2} (Table 5), with 16 % lost as Cu_L and 84 % as Cu_P. Approximately, 10 % of the copper sprayed as BM was washed-off as Cu_L and 50 % as Cu_P. Overall, the dosage had a direct influence on Cu_T and Cu_P ($P < 0.05$ and

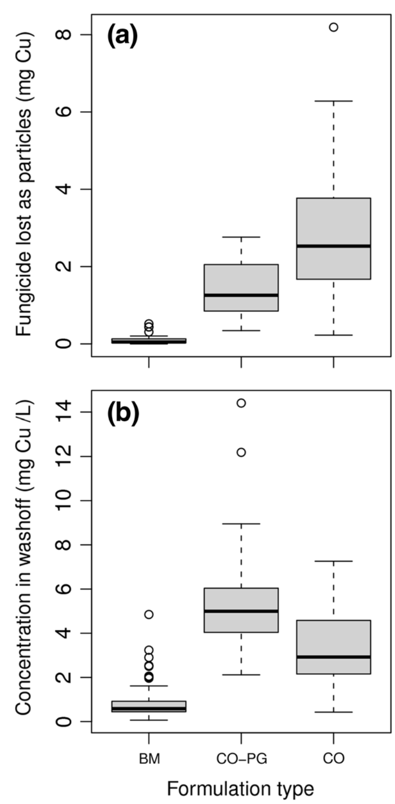

Fig. 4 *Box plot* representation comparing the results of the factor design (12 wash-off runs for each of the three Cu-based fungicides tested). Data are: **a** mass of Cu lost as particles (mg Cu_P) after a run. **b** Total Cu concentration in wash-off (mg Cu_T L^{-1}) after a run. Points are the outliers generated by the contribution of the factor levels

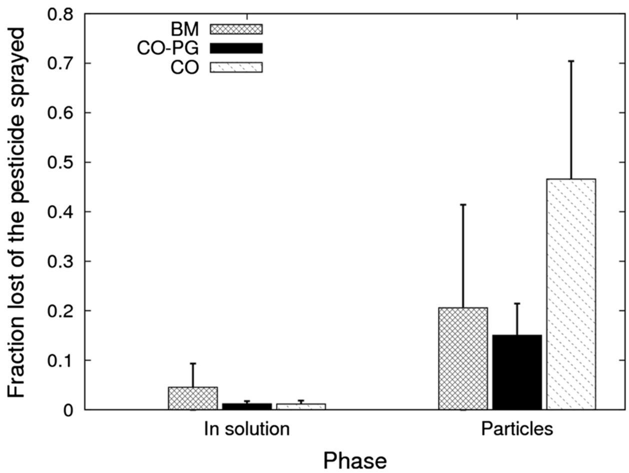

Fig. 5 Phase distribution of fungicide losses comparing the soluble forms and particles in the factor design tests. Data represent the fraction of fungicide lost regarding the total fungicide sprayed on the target for each of the three fungicides. *Error bars* are the contribution of the experimental error plus the effect of the factors

$P < 0.05$), but the factors S and H had no effect. By contrast, the mass of Cu_L was directly related to H ($P < 0.05$) (Table 6a). In addition, Cu_L, Cu_P, and Cu_T decreased with increasing drop size ($P < 0.05$) (Table 6b). The fall height increased the loss of Cu_L ($P < 0.05$), whereas the dosage increased the Cu_T and Cu_P losses ($P < 0.01$ and $P < 0.05$). No interaction between factors was significant (Table 6a, b).

Copper oxychloride wetting powder (CO)

The average total loss (Cu_T) was 87.5 mg Cu m^{-2} (i.e., 35 % of all Cu sprayed), with 7 % (6.4 mg Cu m^{-2}) lost as Cu_L and the remaining 93 % (81.1 mg Cu m^{-2}) as Cu_P (Table 5). The percentage loss was 35 % for Cu_T (2 % for Cu_L and 33 % for Cu_P). The only statistically significant effect on CO losses was D, which increased the mass of Cu_L ($P < 0.05$) and Cu_P ($P < 0.005$) and hence of Cu_T ($P < 0.005$) (Table 6a). The net loss of Cu_L was positively correlated with the interaction $S \times H$ ($P < 0.05$) (Table 6a). The percentage losses (Table 6b) decreased with increasing S ($P < 0.005$), but they increased with D ($P < 0.01$) and the interaction $H \times S$ ($P < 0.05$).

Copper oxychloride colloidal suspension (CO–PG)

The average loss of Cu_T from CO–PG was greater than in the other two fungicides (Table 5). Thus, Cu_T amounted to 165.8 mg Cu m^{-2}, of which 2 % (4.0 mg Cu m^{-2}) was in solution and 98 % (161.9 mg Cu m^{-2}) was particles. The fungicide dosage had a statistically significant positive effect on the mass of Cu washed-off in all fractions ($P < 0.01$) (Table 6a). The percentages of Cu lost in all fractions were positively influenced by D ($P < 0.005$, $P < 0.01$, and $P < 0.01$ for Cu_L, Cu_P, and Cu_T, respectively) and negatively by S ($P < 0.005$, $P < 0.01$, and $P < 0.01$ for Cu_L, Cu_P, and Cu_T, respectively) (Table 6b). The percentage lost in solution was negatively influenced by the interactions $D \times H$ ($P < 0.005$) and $D \times S$ ($P < 0.05$) and was positively correlated with the $S \times H$ interaction ($P < 0.05$). These interactions indicate that small raindrops falling from greater heights reduced loss, which can be explained by aerodynamic artifacts, more height increases the number of drop impacts outside the sprayed area.

Summary of the factor analysis

Fungicide dosage had a strong influence on the Cu_L, Cu_P, and Cu_T losses in the three fungicides (BM, CO, CO–PG) in terms of both mass and percentage. The only exception to this pattern was Cu_L from BM, which may be controlled mainly by the solubilization rate. The drop fall height only affected the release of Cu_L from BM, both in absolute mass terms and in relation to the amount of fungicide applied, possibly due to the mechanical stirring effect of the drop impacting the solubilization of BM. These results suggest increased solubility of BM, which was the formulation with the highest percentage of Cu_L lost. Raindrop size exhibited a significant negative correlation with the entire relative Cu losses (i.e., those referring to the amount of Cu applied). These results suggest that using a larger number of small drops is more efficient than using a smaller number of large drops, irrespective of the fungicide dosage. This conclusion is surprising because one would expect a large drop size and energy to result in greater losses. The number of impacts per surface unit was the factor most strongly influencing Cu losses.

Table 5 Summary of copper losses resulting from factor analysis of wash-off using the single-drop rainfall simulation

Fungicide	Total	Soluble	Particulate
BM	7.3 ± 7.3	1.2 ± 1.2	6.1 ± 3.7
CO	87.5 ± 39.7	6.4 ± 2.7	81.1 ± 39.6
CO–PG	165.8 ± 97.7	4.0 ± 2.2	161.9 ± 96.7

Data represent the constant terms of the factorial model. Data are expressed in mg Cu m^{-2} sprayed surface (mean ± standard deviation)

Table 6 Statistical significance of the influence of the factors and their interactions (A) on the mass of Cu lost and (B) on the percentage of Cu lost in factor analysis

	Soluble			Particulate			Total		
	BM	CO	CO–PG	BM	CO	CO–PG	BM	CO	CO–PG
(A) Total mass of copper lost									
S									
H	* (+)								
D		* (+)	** (+)	* (+)	*** (+)	** (+)	* (+)	*** (+)	** (+)
D × H			*** (−)						
H × S		* (+)	* (+)						
D × S									
(B) Percentage of copper lost									
S	* (−)	*** (−)	*** (−)	* (−)	*** (−)	** (−)	* (−)	*** (−)	** (−)
H	* (+)								
D		** (+)	*** (+)	* (+)	** (+)	** (+)	** (+)	** (+)	** (+)
D × H			*** (−)						
H × S		* (+)	* (+)						
D × S			* (−)						

S drop size, *H* falling height, and *D* fungicide dosage

Signification levels correspond to the different fractions for each fungicide. Signification levels $P < 0.005$ ***; $P < 0.01$ **; and $P < 0.05$ *. The sign after signification levels indicates increasing of Cu loss (+) or decreasing loss (−)

Factor interactions were generally less significant than the individual factors. Unlike the sheet-flow system used by Paradelo et al. (2008), the raindrop impact used here precluded the development of a model for quantitative modeling of factors to predict the Cu losses. Copper fractionation in the wash-off water produced by the drops indicated that most of the copper was lost as particles. The Cu_P loss was slightly sensitive to the raindrop impact energy. The % Cu_P lost in wash-off experiments imposing sheet flow (Paradelo et al. 2008) was greater than in our raindrop experiments. These differences suggest that sheet flow is more effective in the detachment of loose attached particles than the raindrop impacts. The lack of statistical significances in the raindrop size and fall height factors used here resulted from the range of energy levels of raindrop impacts not being wide enough to have a significant effect on Cu losses. Our results suggest that the detachment power of small raindrops with 1 m fall height largely exceeds the attachment strength of a significant percentage of fungicide particles. The lack of sensitivity of raindrop impact power in the detachment of the particles in the factor analysis agreed with the results of the loss kinetics, and the SEM images that showed accumulation of loosely attached particles at the border of the traces of droplets.

Conclusion

Losses in wash-off of three Cu-based fungicides formulations were modeled with a physically based stochastic approach. The model reproduced quite well the wash-off losses in experiments using un-reactive testing surfaces previously sprayed with the fungicides. Good fittings were obtained by assuming a two-level raindrop detachment performance model that reproduces the variability in the observed loss in the wash-off. Model fitting parameters can estimate the detachment unit area surface per impact, the number of repeated impacts in the same locations producing losses until the exhaustion, and mass of detached per impact. Two mechanisms control the loss of Cu-based fungicides in wash-off under simulated rainfall: detachment of particles and solubilization of non-rainfast particles. In general, the impact power has less influence in the high performance level than in the low performance level.

The traditional Bordeaux mixture exhibited smaller Cu_T loss than the other two copper-based formulations. Drop size and fungicide dosage strongly influenced the percent losses. The percentage of Cu lost decreased with increasing drop size and dosage was the most influential factor in the three formulations, especially on Cu_P. The impact energy of raindrops exceeds that required to produce the release of fungicide as particles. This is in good agreement with the loose arrangement of the fungicide particles seen in the SEM images. Surprisingly, the amount of soluble forms depends on the kinetic energy of raindrop impact. The model cannot predict the particulate/soluble loss ratio because both the detachment of non-rainfast particles and the solubilization of rainfast pesticide did not show a clear dependence on the mechanical energy of raindrops. Based on this approach, a model can be scaled up to analyze fungicide losses in crop fields by using the drop size spectra, intensity, and duration of typical rainfall events.

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